# THE CHLORIDE CONTENT OF RUN-OFF WATER DUE TO STREET DEICING

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by

Dennis Paul Day, Sr.

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Dennis Paul Day, Sr.

Approved by Committee:

F. Emmitt Jakob
Chairman

Robert L. Ledbetter

Wayne B. Mackey

Earle L. Canfield
Dean of the School of Graduate Studies

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# INTRODUCTION

The element chlorine is a member of the halogen group. Some of the other important elements in this group are fluorine, bromine and iodine. Generally chlorine exists in the highest concentrations, and is the most widely distributed of the halogens in natural occurring bodies of water. Its presence in water usually takes the form of the chloride ion, $Cl^-$ (7). The chloride ion is present in natural waters in low concentrations (4). Exceptions occur where streams receive inflows of high-chloride waters such, as ground water, industrial and domestic wastes, and in some coastal regions where intrusions of sea water are a possibility.

Precipitation in all areas, particulary close to the oceans, contains a few milligrams of chloride per liter (5). The concentration of the chloride decreases rapidly in a landward direction. Precipitation shows some seasonal variation in chloride concentration due to wind direction and velocity (5). The over all average of chloride concentration in precipitation throughout the United States is quite low. Concentrations of less than five-tenths of one milligram per liter are common (6).

Fisher, in a study of a North Carolina watershed, pointed out that the chloride contributed to the surface water by precipitation accounts for only about one-fourth of the chloride present. Fisher indicated that the remaining chloride can be explained in terms of human activities

involving the use of salt (5).

Ordinary sewage contributes to the chloride concentration in streams and rivers where treated or untreated wastes are being dumped. Sewages can also cause ground water contamination in certain unfavorable conditions. The treatment of municipal water supplies with chlorine to kill organisms existing in the water source and the treatment of sewage plant effluents with chlorine can be considered minor sources of the chloride ion which is carried by surface water.

The chloride ion itself is not considered objectionable in concentrations less than about 250 milligrams per liter (at such concentrations a salty taste can be noticed in waters containing sodium ion) (1). The presence of high concentrations of chloride or increasing concentrations does, however, give reason to suspect sewage contamination of the water being tested (8). For this reason public works departments, municipal water works, sewage treatment plants, and state and local health organizations monitor the water near populated areas for chloride concentrations.

Street deicing may also be one of the factors contributing to the chloride concentrations in surface water. Some cities use large quantities of salt to speed ice and snow removal. There presently are some studies being conducted that are trying to determine the effects of

street and road salting on the quality of the water in the rivers and streams draining areas that receive frequent saltings.

In one of these studies, Blaser has determined that deicing salts are not contaminating major waterways that have large water flow volumes. This study has found, however, that deicing salts can cause the increase of chloride levels in ponds, small lakes, and streams (3).

The purpose of this investigation will be to try to establish any relationship that exists between municipal street deicing and the chloride content of the run-off water from the city of Des Moines, Iowa.

## METHOD

The Des Moines River joins one of its tributaries, the Raccoon River, within the city of Des Moines. The larger of the two rivers, the Des Moines, enters the city from the north. The smaller, the Raccoon, enters the city from the west and joins the Des Moines River near the Des Moines business district at the Scott Street Dam (see Figure 1).

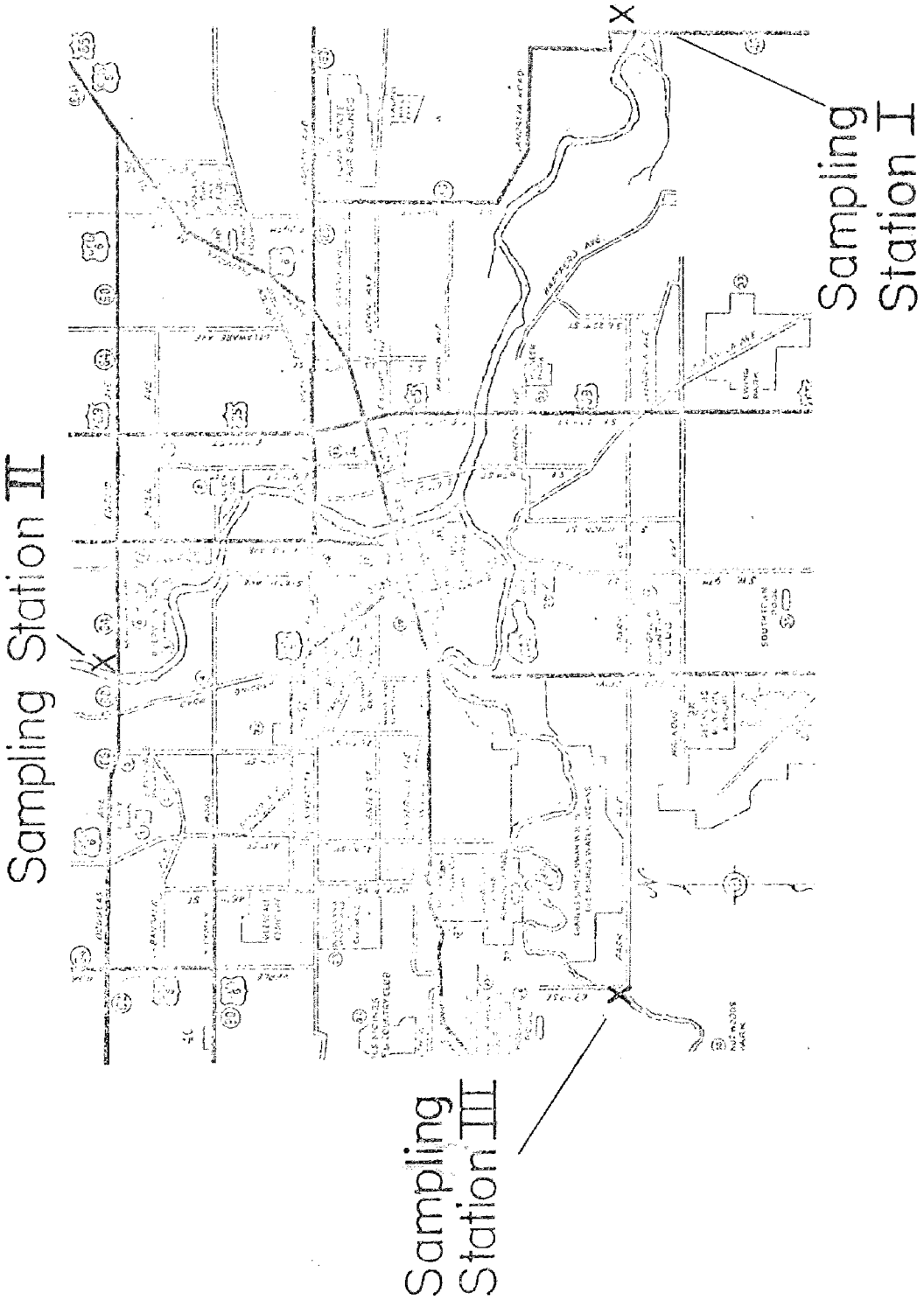
A very high percentage of the excess surface water from the city enters the Des Moines River within the Des Moines city limits. Thus the river just downstream from Des Moines should reflect the quality of the city's run-off water.

From December 2, 1970 to April 1, 1971 water samples were taken from the surface of the rivers at three different locations. Two locations on the two major waterways flowing into the city (the Des Moines and the Raccoon Rivers) and one location on the Des Moines River which is the major river flowing from the city (see Figure 1).

Collection station number I was located on the Des Moines River at the Highway 46 bridge. This bridge is commonly called the IPALCO bridge. The samples were taken from the north side of the river about 40 yards downstream from the bridge, sampling was done every four days during the evening hours, normally between 4:00 p.m. and 6:00 p.m. (see Figure 1).

Figure 1

Location of Sampling Stations



Collection station number II was located on the Des Moines River at the Des Moines Euclid Avenue bridge. Samples were taken from the east bank of the river about 30 yards upstream from the bridge every four days between 6:00 p.m. and 8:00 p.m. (see Figure 1).

Collection station number III was located on the Raccoon River at the Des Moines 63rd Street bridge. The sampling was done from the south river bank about 30 yards, upstream from the bridge every four days usually between 4:30 p.m. and 7:00 p.m. (see Figure 1).

The samples at all three locations were taken from the surface of the river. When the rivers were frozen, the samples were taken through the ice from moving water. This was done by drilling a hole in the ice and lowering the container to where the water could be reached. Sampling at all three stations was carried out on the same day, starting with station I then progressing to stations III and II respectively (see Figure 1).

All of the samples were taken in clean glass containers that had been rinsed in the water being sampled. The rinsing was done just prior to taking the actual sample. The samples were then carefully labeled, sealed and stored until analyzed.

The conductivity of water at each of the three stations was checked by a Beckman Conductance meter. Many samples were taken from both the surface and from

various depths to determine the homogeneity of the river at these locations.

## ANALYSIS

The method of analysis decided upon for the determination of the chloride concentration was the Mohr method (1). This method is based upon the following reactions in a neutral solution: The first is the reaction of the silver ion, Ag+, supplied by the known solution of silver nitrate, $AgNO_3$, with the chloride ion, $Cl^-$, supplied by the unknown solution, forming a very insoluble precipitate, silver chloride, AgCl (2).

$$Ag^+ + Cl^- \longrightarrow AgCl \qquad (1)$$

The second reaction is the reaction of the chromate ion, $CrO_4^=$, with the excess silver ion, $Ag^+$, to form a red precipitate of silver chromate, $Ag_2CrO_4$ (2).

$$2Ag^+ + CrO_4^= \longrightarrow Ag_2CrO_4 \qquad (2)$$

The silver chloride is quantitatively precipitated before the permanent formation of silver chromate (1).

The substances that normally interfere with the Mohr method are usually not present in sufficient quantity to interfere. The presence of any of the other halogens will be indicated as equivalents of chloride. The presence of orthophosphates in excess of twenty-five milligrams per liter interferes by precipitating as silver phosphate, $Ag_3PO_4$ (1).

The precision of the Mohr method stated in the literature is ± 1.7 milligrams per liter (1). A short study of the end point error and precision of the method used

in this experiment indicates that precision of the method is nearer to a value of ± 1 milligrams per liter (see APPENDIX I).

The determination of chloride in each sample was determined by taking four 50 milliliter aliquots by pipet from each sample. These were titrated with the standard silver nitrate solution and the results averaged. The concentration of chloride was determined in accordance with the equation,

$$MgCl^{-}/Liter = \frac{(A - B) \times N \times 35{,}450}{ml\ sample} \qquad (3)$$

where A = ml titration for sample, B = ml titration for blank, and N = normality of silver nitrate (1).

The concentrations of chloride found at each of the three sampling locations are shown in Figures 2, 3 and 4. The values for the concentration of chloride in milligrams per liter were used with the river flow data as shown in Figures 5, 6 and 7 to determine the actual quantities of chloride being carried by the river at these locations. These quantities were determined using the following equation,

$$\frac{M \times F \ \frac{\text{cubic feet}}{\text{second}} \times D \ \frac{\text{pounds}}{\text{cubic foot}}}{10^{6}} = Cl^{-} \ \frac{\text{pounds}}{\text{second}} \qquad (4)$$

where M = the concentration of chloride in parts per million, F = the discharge of the river, and D is the density of water.

Figure 2

Chloride Concentration at Station I

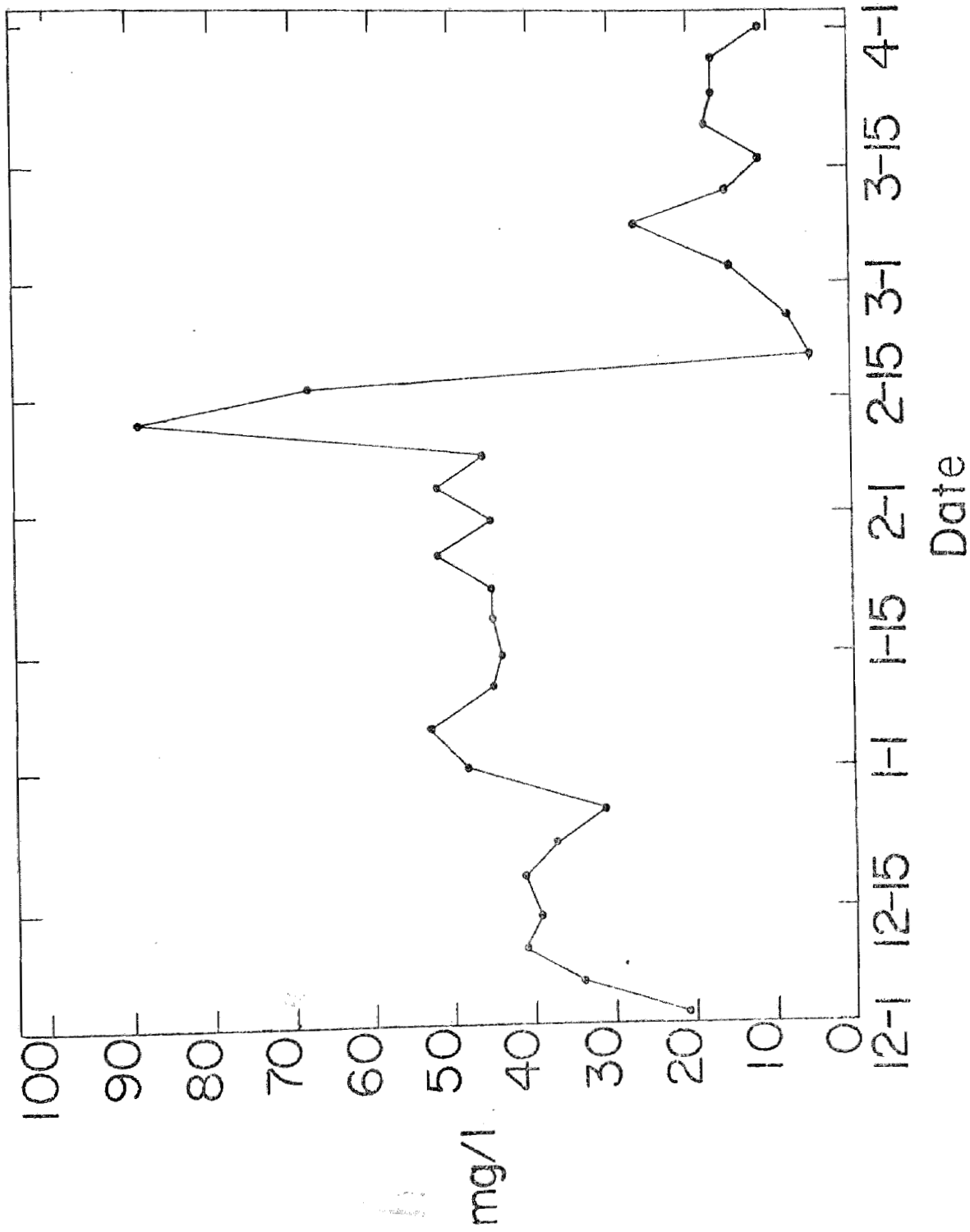


Figure 3

Chloride Concentration at Station II

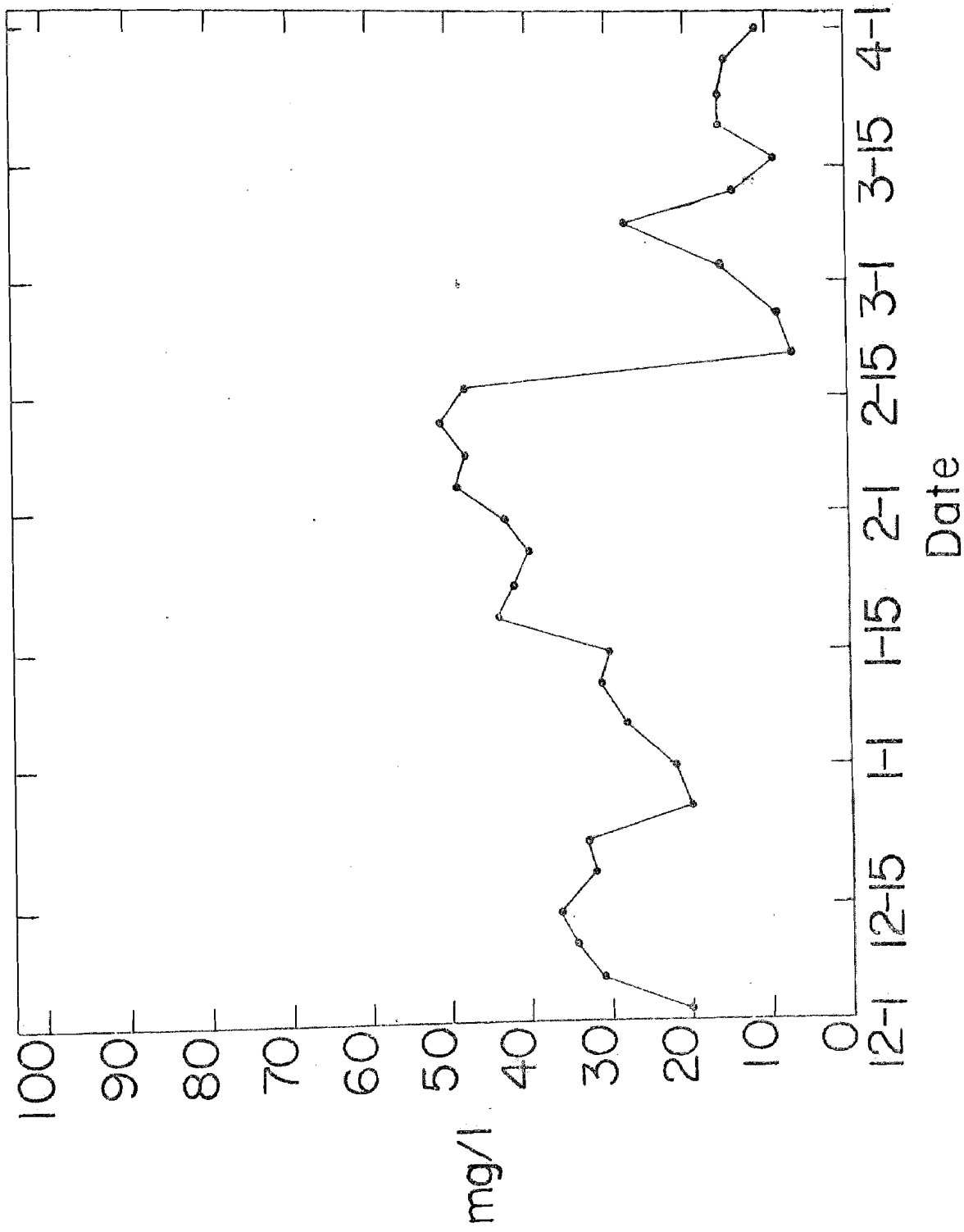


Figure 4

Chloride Concentration at Station III

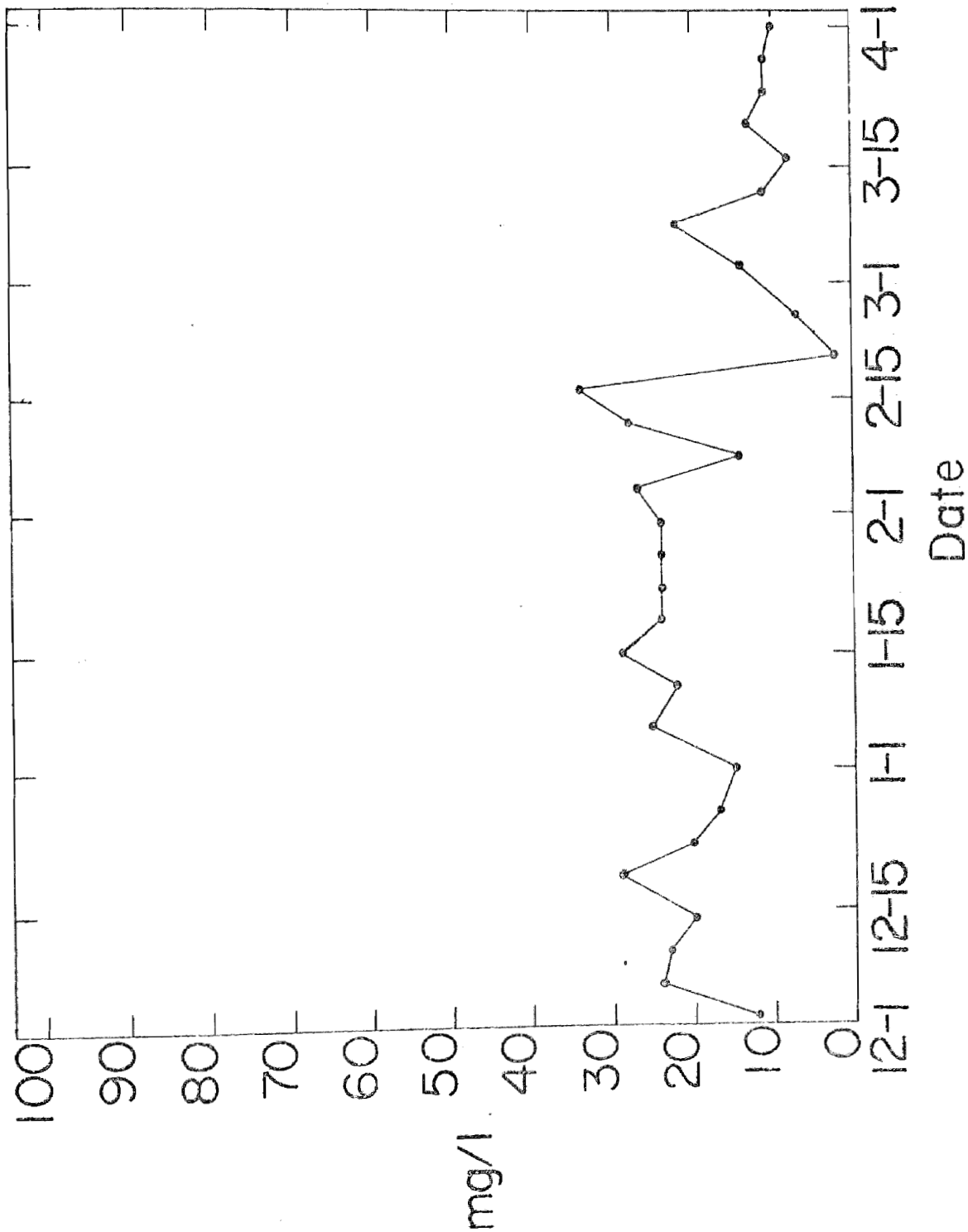


Figure 5

River Flow at Station I

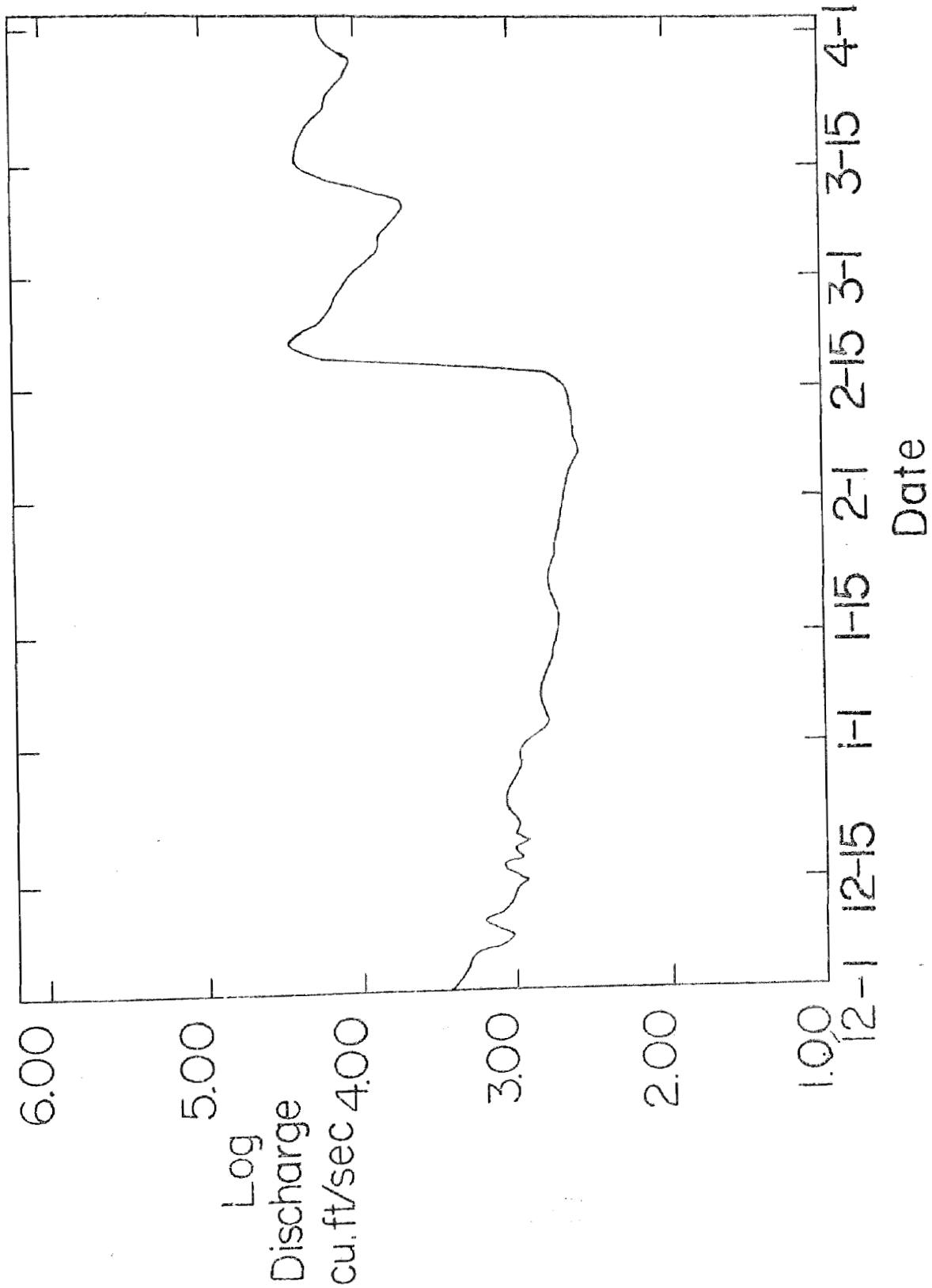


Figure 6

River Flow at Station II

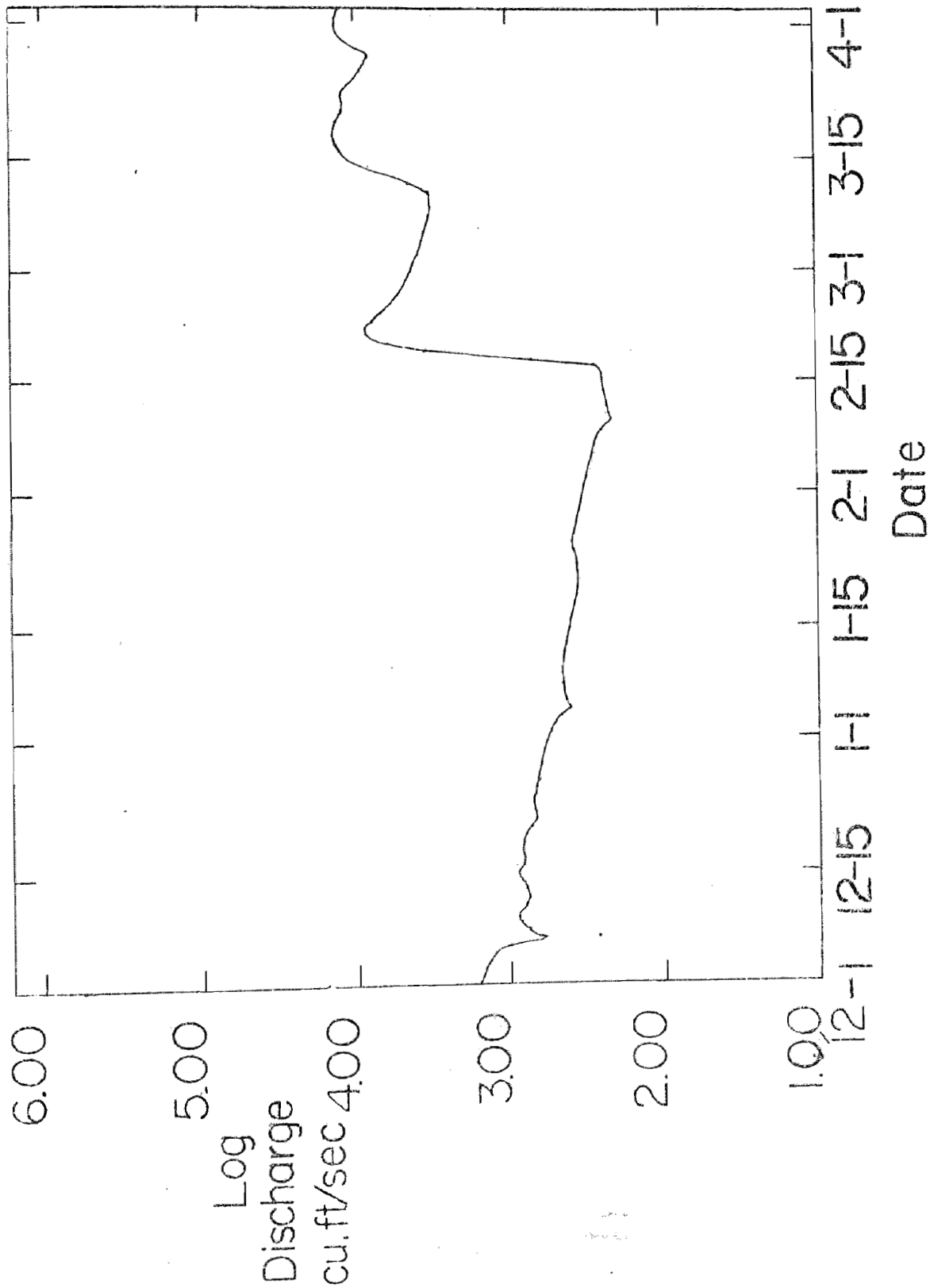
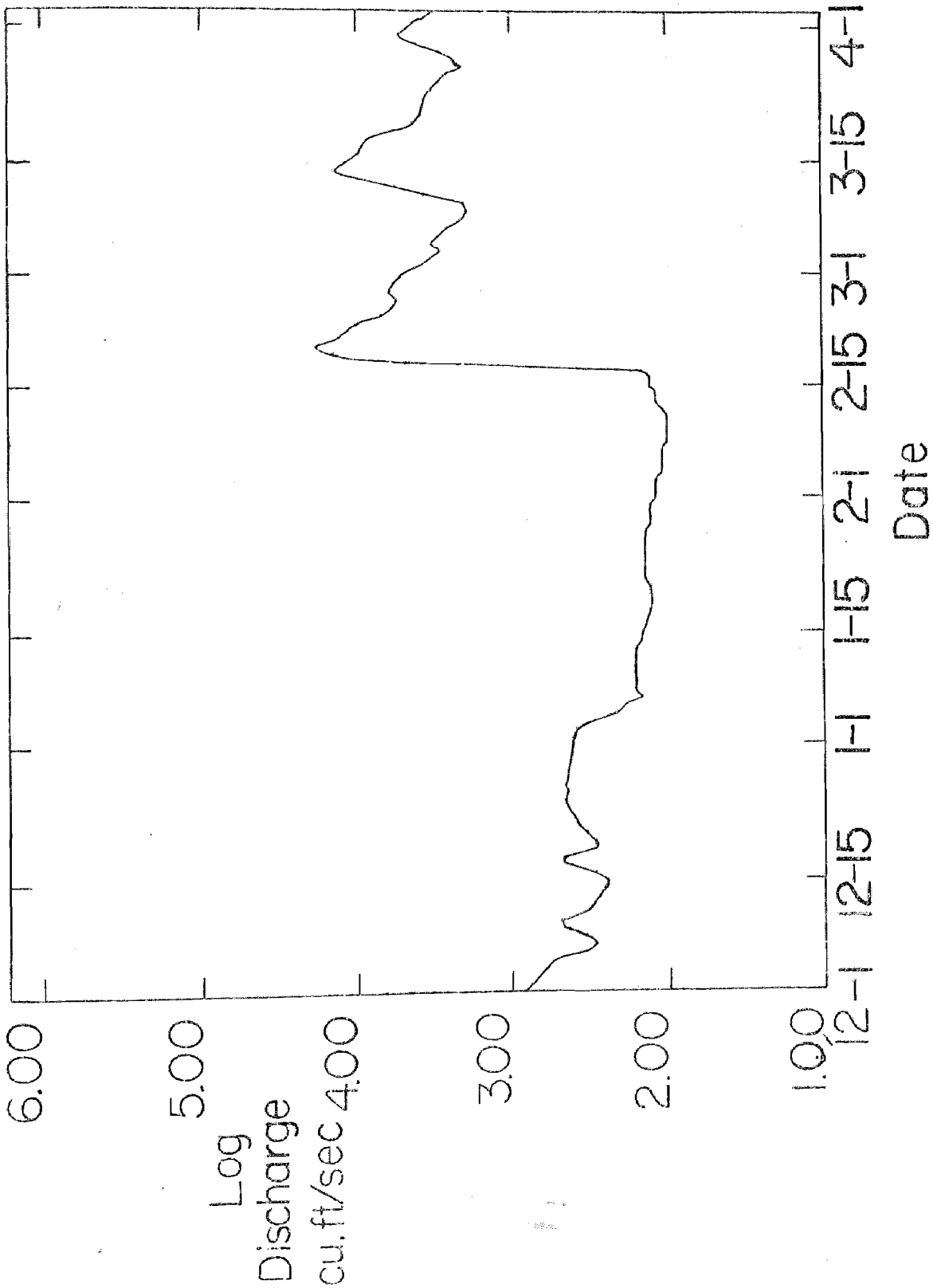


Figure 7

River Flow at Station III



The values of chloride in the river at each of the three stations are shown in figures 8, 9 and 10.

The weight of the chloride ion contributed to the river by the city of Des Moines was determined, by subtracting the chloride amounts observed entering the city by river from the amounts of chloride detected flowing out of the city, in the river. This quantity is referred to as the "chloride gain" and is shown in figure 11.

Daily maximum temperatures and snowfall information obtained from local climatological data are shown in figures 12 and 13.

The dates and amounts of street salting by the city of Des Moines were obtained from the Streets Department and are shown graphically in figure 14.

Figure 8

Chloride Load at Station I

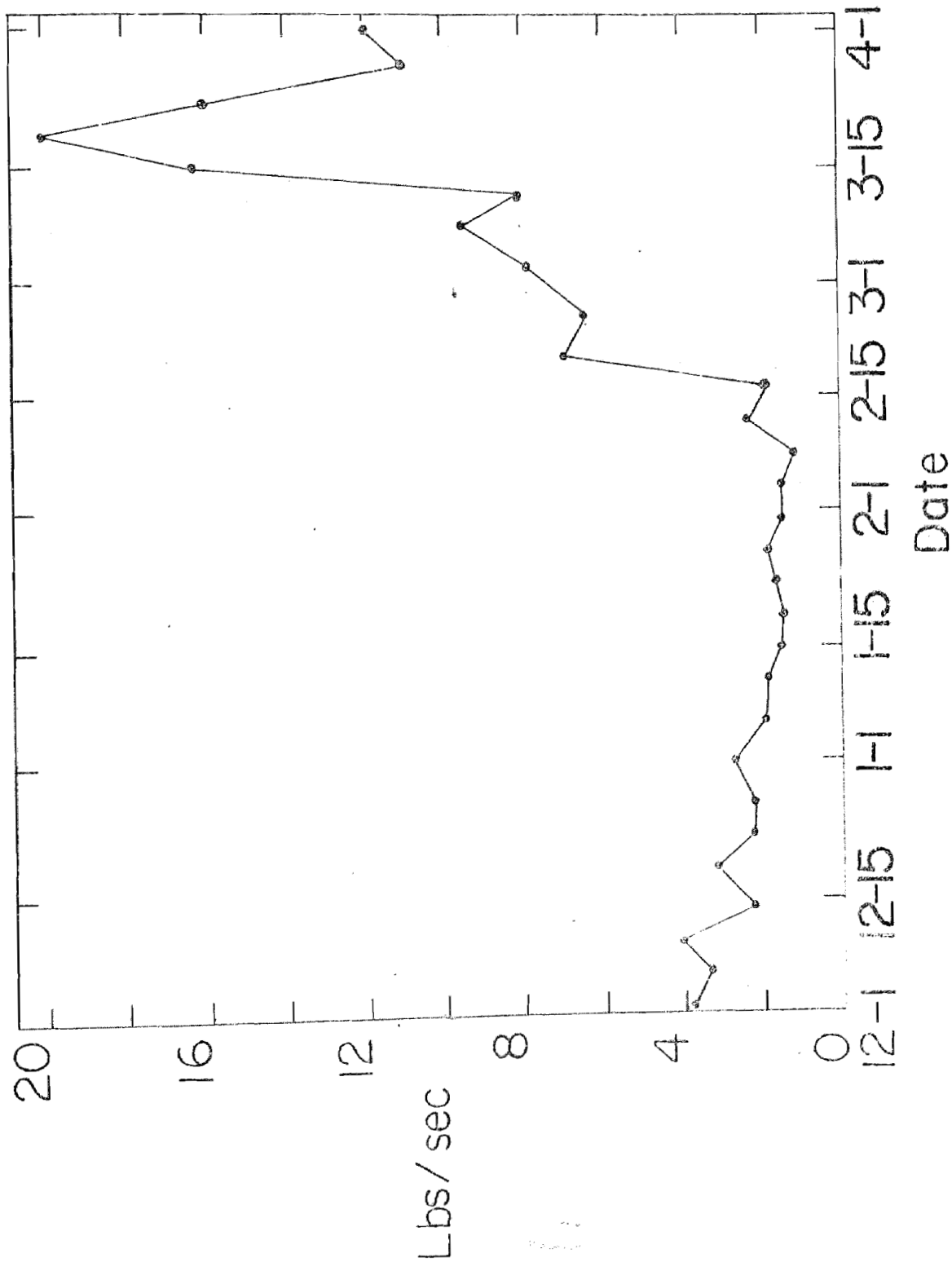


Figure 9

Chloride Load at Station II

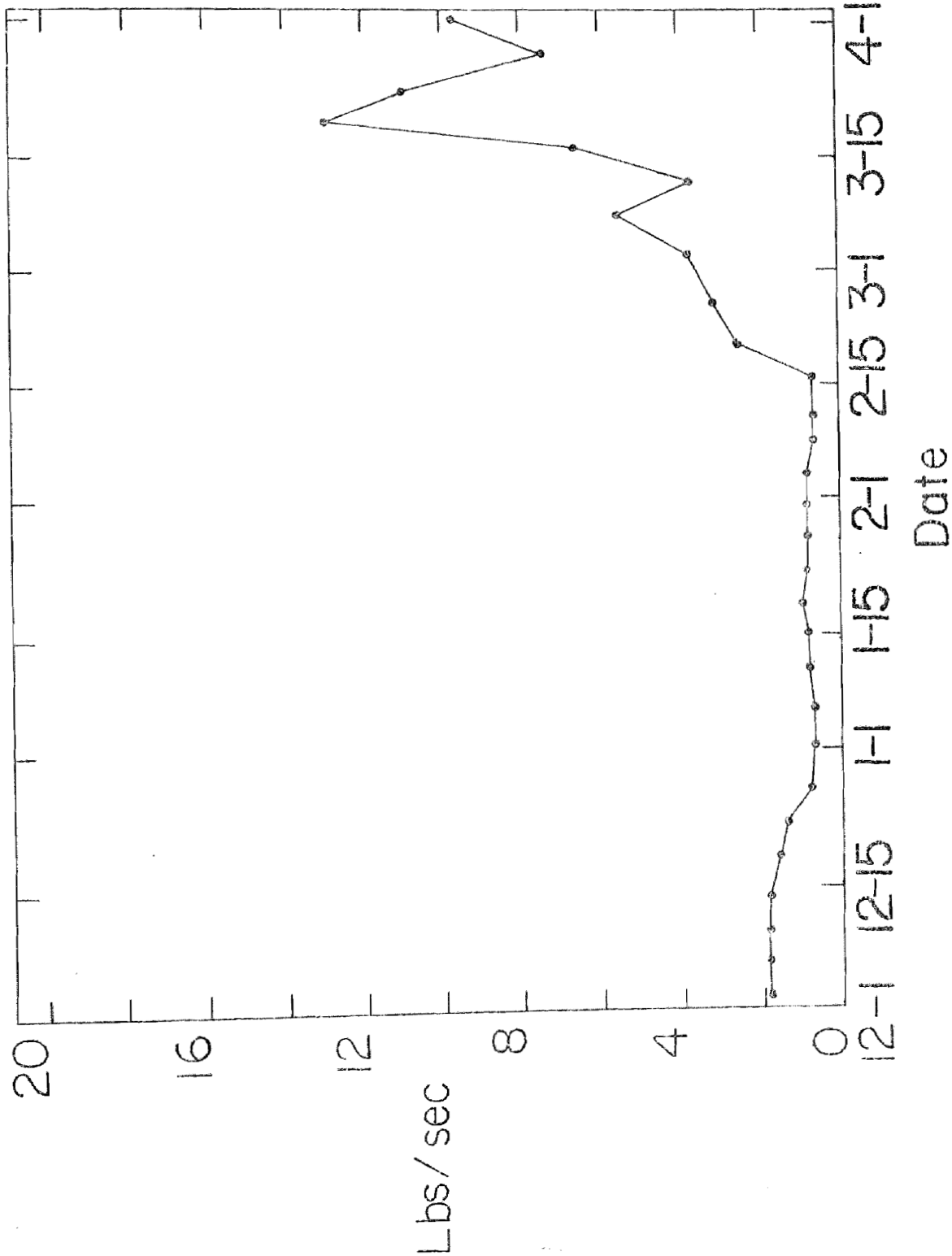


Figure 10

Chloride Load at Station III

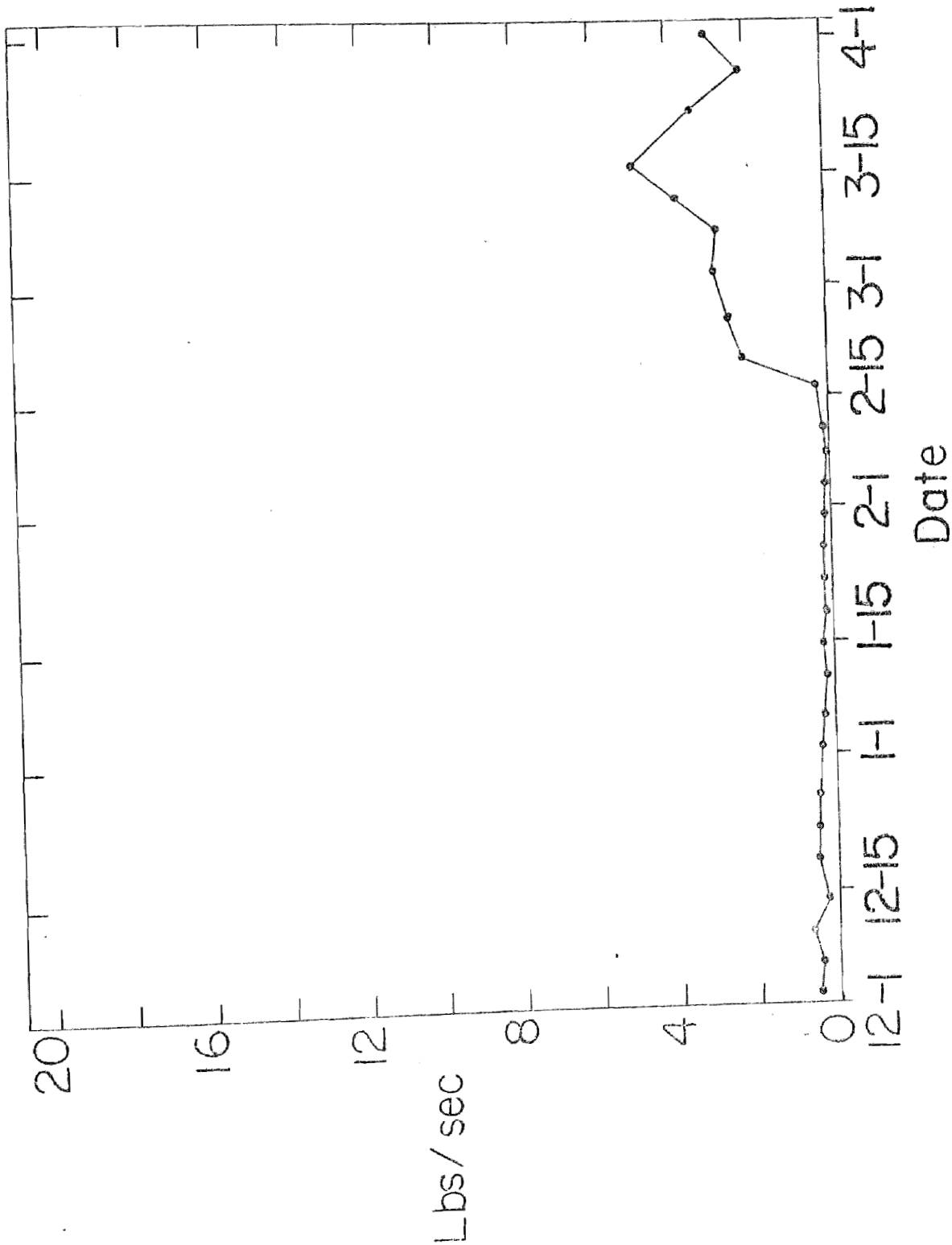


Figure 11

Chloride Load Gained by the River

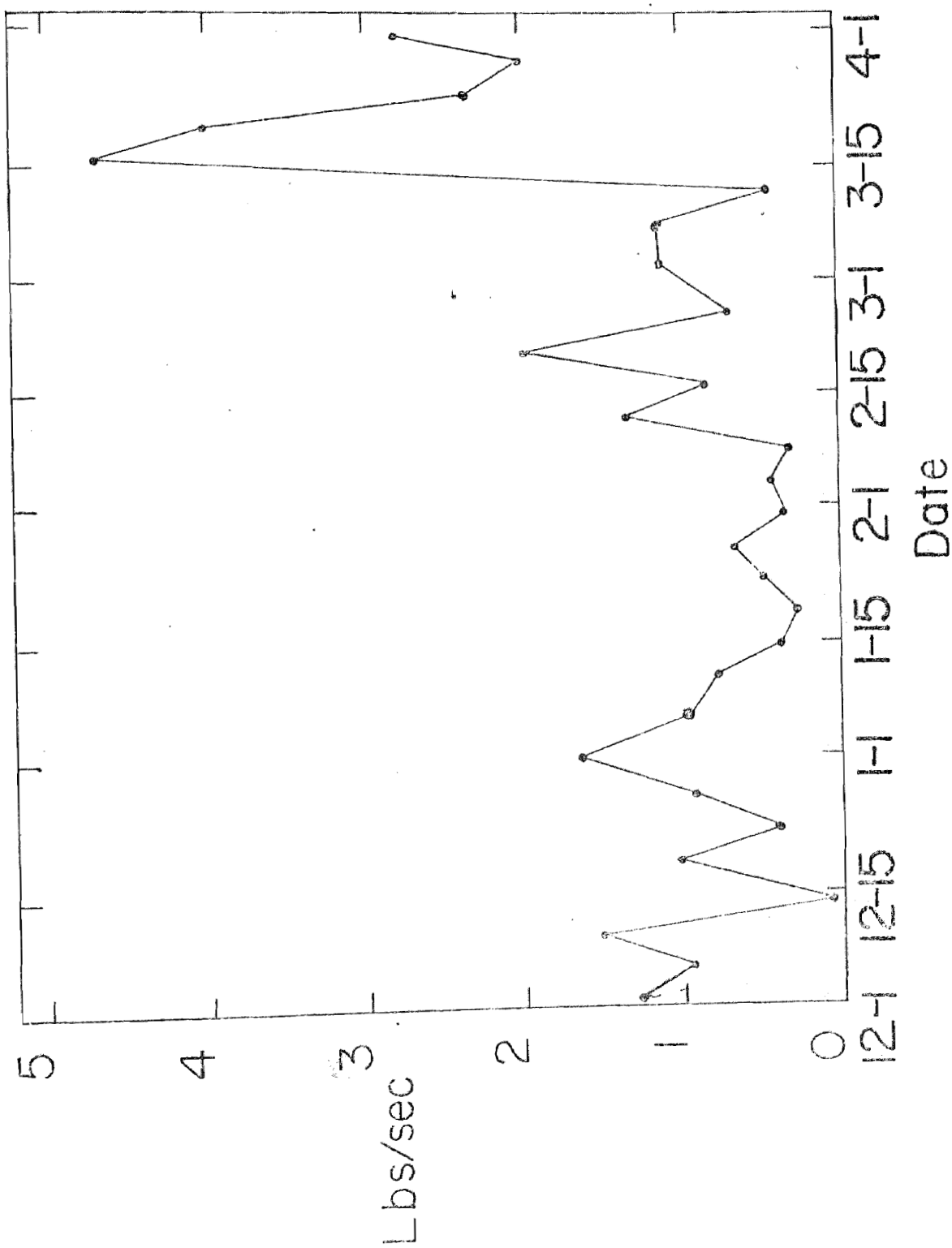


Figure 12

Maximum Daily Temperature

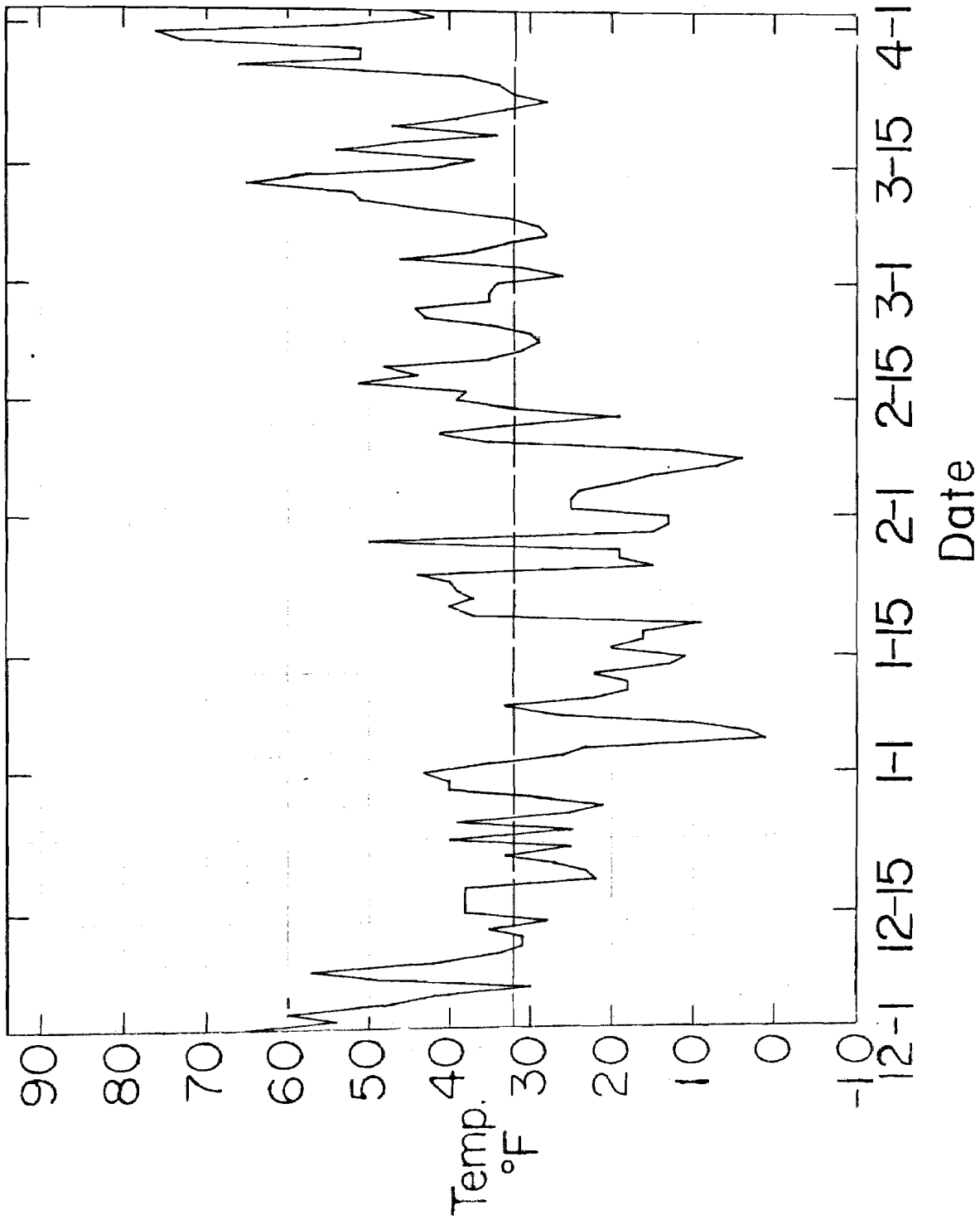


Figure 13

Snow Accumulation

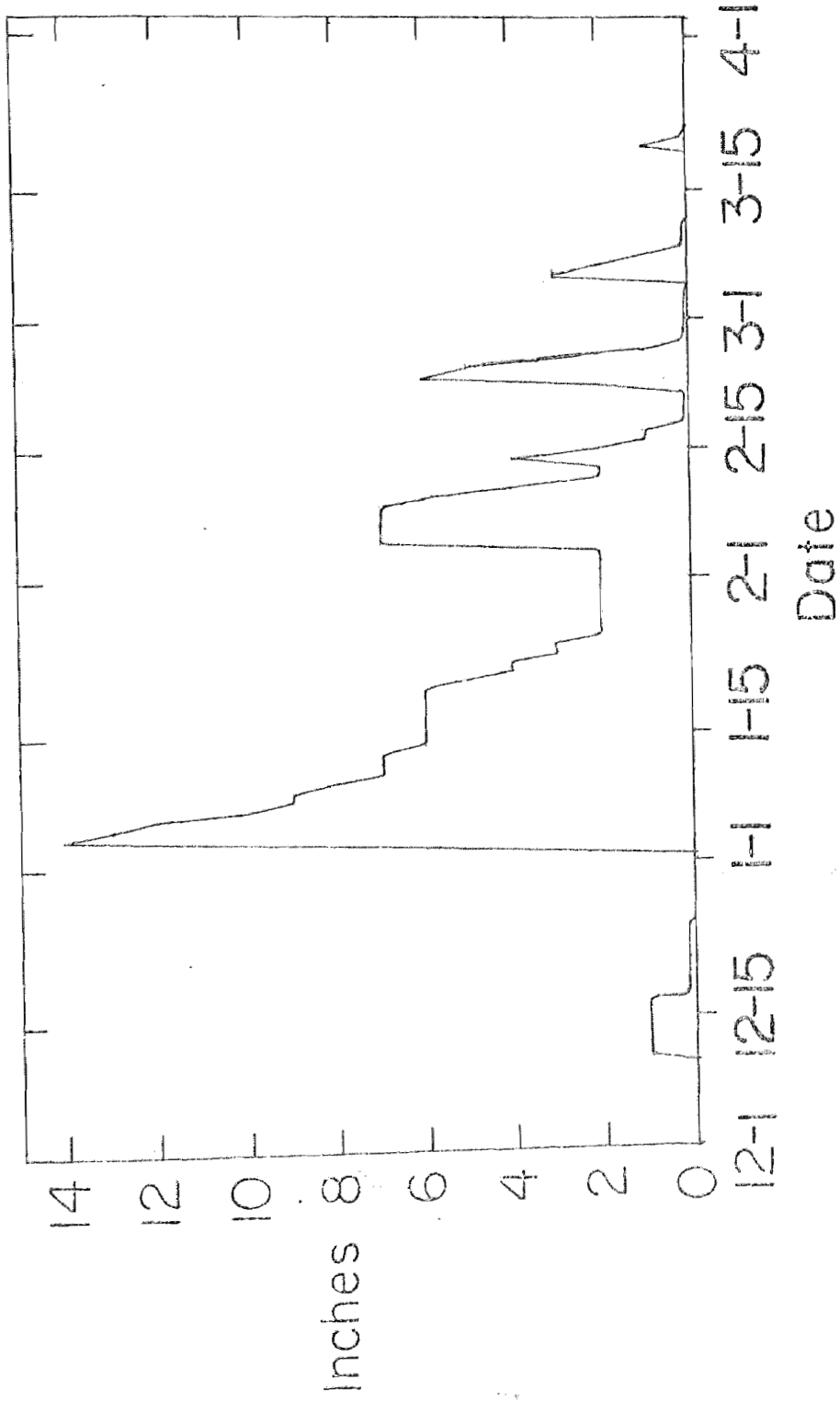
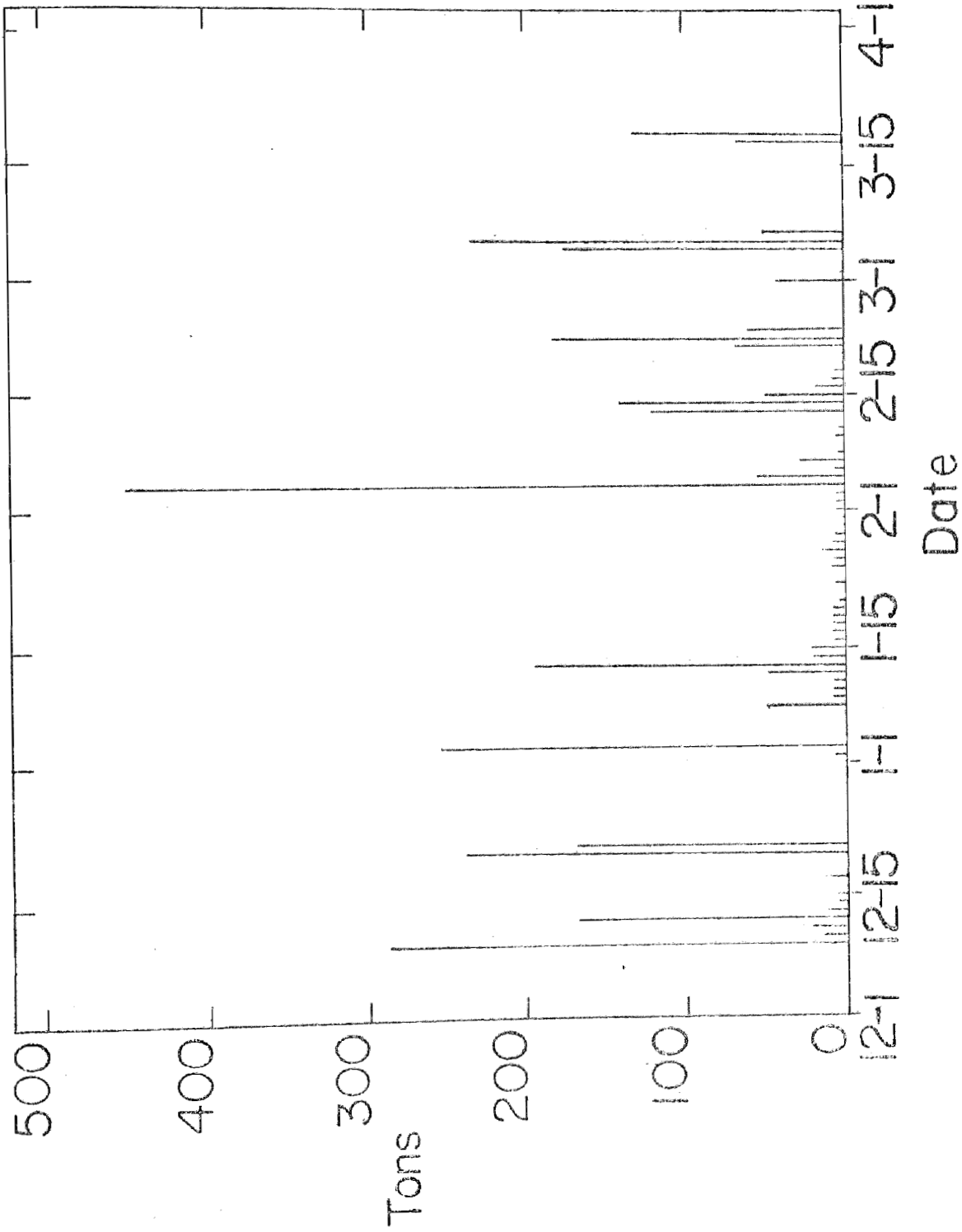


Figure 14

Dates and Amounts of Street Salting



## DISCUSSION

The water in the river at the three sampling locations was remarkably well mixed. The only exception was the water on the surface of the river at station I. The meter could not be balanced when the electrodes were placed directly into the water near the boundary of the hot water being released by Iowa Power and Light Company and the cooler river water. However, when a sample of this water near the boundary was taken from the river and tested in the container the conductance bridge indicated that the water in this area contains the same amount of dissolved solids as the other parts of the river. The variance of the meter was probably due to rapid water temperature changes near the boundary of the hot water.

The concentration of chloride at all three sampling stations exhibited similar characteristics (see Figures 2, 3 and 4). The concentration generally increased as the river flow decreased (see Figures 5, 6 and 7). The maximum concentrations being reached just before the big increase in river flow which came in the middle of February. It should be noted that the maximum concentrations are far below the maximum of 250 milligrams per liter allowable concentration for drinking water (1).

It is apparent that the concentration of chloride in the river at all three stations shows little if any direct relationship with temperature (see Figures 2, 3, 4 and 12).

The actual chloride contained in each of the rivers at the sampling location increases significantly in the early part of February and increases still more in March (see Figures 8, 9 and 10). Other river flow at each of these stations also increase at about the same times in February and March (see Figures 5, 6 and 7). This indicates that there is a correlation between river flow and the quantity of chloride carried by the river.

The chloride contributed to the river by Des Moines comes from two sources. They are the sanitary sewers and the storm sewers which carry the run-off water. The total chloride gained is greater in almost all instances than the average chloride contribution due to the sanitary sewer effluent. The chloride gained compared to the maximum daily temperature indicates that there is a good correlation existing between them (see Figures 11 and 12). The increase in chloride gained, in all cases follows a general temperature gain by one to three days. The time lag between temperature and the chloride gain probably would have been more consistant if the river were sampled more frequently.

The large peak in chloride gain occurring in the first part of March can be partially explained as the probable result of two different effects.

The city, in the course of snow removal, dumps the snow, which had been removed from the business district, along the west bank of the river just north of the University

Avenue Bridge (see Figure 1). The snow is not dumped directly in to the river, but is dumped on the river side of the flood control levy. This pile of snow contains much of the salt that had been spread on it before the snow could be removed from the streets. When the river level is high enough to reach this stockpiled snow the salt contained in it will be released causing a chloride gain during that period of high water.

The amounts of salt used on the streets depend on the amounts of snow. The deep snows, those over about three inches, usually are removed by mechanical means while lesser accumulations are often removed by salting.

The last snow that was salted amounted to about one inch and occurred on the 19th of March (see Figure 13). The quantity of salt used on that snow in a two daymelting period was about 200 tons (see Figure 14). The largest snow of the winter fell on the second and third of January (see Figure 13). The quantity of salt used on that snow in a 20 day melting period was about 700 tons (see Figure 14).

The ratio of the tons of salt used to the inches of snow are approximately 700/14 or 50 tons of salt for each inch of the fourteen inch snow, and 200/1 or 200 tons of salt for the one inch snow. It is apparent that, while there was less salt used on the one inch snow the concentration of salt is approximately 4 times the concentration of the salt on the 14 inch snow.

Assuming that the salt contained in the run-off water is evenly distributed over the melting time of the snow, the 14 inch snow could contribute approximately 35 tons of salt per day to run-off water. Under similar circumstances the one inch snow could contribute 100 tons of salt per day to run-off water during its two day melting period.

It is possible, indeed probable, that for a short period of time the salt used on the one inch snow contributed chloride to the run-off water at a rate almost three times as large as did the 14 inch snow.

## SUMMARY

The use of sodium chloride as a street deicer by the city of Des Moines did not effect the chloride concentration of the Des Moines River in the winter of 1970-71. However, there is some evidence that street salting does effect the salt load of the river.

## SUGGESTIONS FOR FURTHER STUDY

(1) A study of the chloride content of the river as related to street deicing, using a monitor that would give continuous data on chloride concentration.

(2) A study of the effects of the heat released to the Des Moines River by Iowa Power and Light Company.

(3) A study of the chloride concentration in Fourmile Creek and its relationship to street salting in Ankeny, Iowa.

(4) A study of the chloride concentration of some wells near highways or other areas that get salted on a regular basis.

# APPENDIX I

## END POINT ERROR

The known silver nitrate $AgNO_3$ standard, and the known sodium chloride, NaCl solutions were carefully made by drying and weighing the two reagents to the nearest 0.1 milligram and dissolving them in a small quantity of distilled water and diluting them to volume.

The standard $AgNO_3$ was titrated against many known concentrations of chloride to determine the error in the end point determination.

The theoretical end point values were subtracted from the actual end point values to obtain the error in the end point.

The graph was used to determine all of the end point corrections for the chloride determinations in this investigation.

It is evident from the graph in figure 15, that the end point error is directly related to the concentration of chloride ion.

TABLE 1

DETERMINATION OF END POINT ERROR

| Known $Cl^-$ mg/l | Experimental End Point ml of $AgNO_3$ | Theoretical End Point ml of $AgNO_3$ | End Point Error ml of $AgNO_3$ |
|---|---|---|---|
| 300 | 51.01 | 50.00 | 1.01 |
| 150 | 25.86 | 25.00 | .86 |
| 100 | 17.39 | 16.67 | .72 |
| 75 | 13.16 | 12.50 | .66 |
| 60 | 10.63 | 10.00 | .63 |
| 50 | 8.97 | 8.33 | .64 |
| 30 | 5.60 | 5.00 | .60 |
| 25 | 4.74 | 4.17 | .57 |
| 20 | 3.84 | 3.33 | .51 |
| 10 | 2.15 | 1.67 | .48 |
| 0 | .47 | 0.00 | .47 |

Figure 15

End Point Error

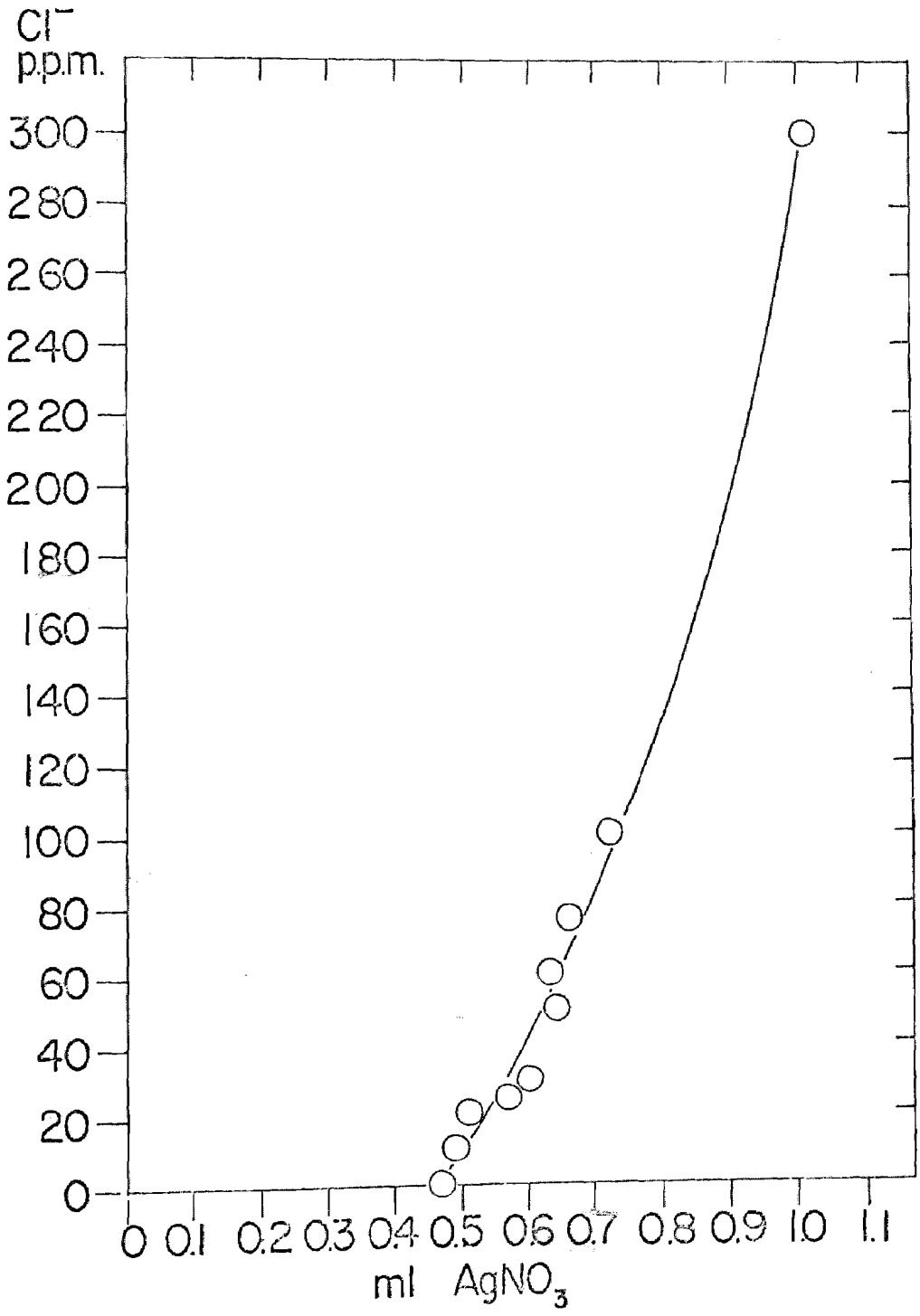


TABLE 2

RIVER DATA STATION I

| | Mg. $Cl^-$ / Sec. | Discharge $Ft.^3$/Sec. | Discharge Lbs./Sec. | Lbs. $Cl^-$ / Sec. |
|---|---|---|---|---|
| Dec. 2 | 21 | 2 510 | 156 624 | 3.8 |
| 6 | 34 | 1 600 | 99 840 | 3.4 |
| 10 | 41 | 1 620 | 101 088 | 4.1 |
| 14 | 39 | 945 | 58 968 | 2.3 |
| 19 | 41 | 1 250 | 78 000 | 3.2 |
| 23 | 37 | 1 010 | 63 024 | 2.3 |
| 27 | 31 | 1 160 | 72 384 | 2.2 |
| Jan. 1 | 48 | 920 | 57 408 | 2.8 |
| 6 | 53 | 600 | 37 440 | 2.0 |
| 11 | 45 | 670 | 41 808 | 1.9 |
| 15 | 44 | 570 | 35 568 | 1.6 |
| 19 | 45 | 530 | 33 072 | 1.5 |
| 23 | 45 | 590 | 36 816 | 1.7 |
| 27 | 52 | 560 | 34 944 | 1.8 |
| 31 | 45 | 520 | 32 448 | 1.5 |
| Feb. 4 | 52 | 470 | 29 328 | 1.5 |
| 8 | 46 | 410 | 25 584 | 1.2 |
| 12 | 89 | 410 | 25 584 | 2.3 |
| 16 | 68 | 430 | 26 832 | 1.8 |
| 20 | 5 | 22 000 | 1 372 800 | 6.9 |
| 25 | 8 | 12 800 | 768 720 | 6.4 |

TABLE 2 - continued

RIVER DATA STATION I

| | Mg. $Cl^-$ / Sec. | Discharge $Ft.^3/Sec.$ | Discharge Lbs./Sec. | Lbs. $Cl^-$ / Sec. |
|---|---|---|---|---|
| Mar. 3 | 15 | 8 450 | 527 280 | 7.9 |
| 8 | 27 | 5 630 | 371 312 | 9.5 |
| 12 | 15 | 8 650 | 539 760 | 8.1 |
| 16 | 11 | 23 800 | 1 485 120 | 16. |
| 20 | 18 | 18 300 | 1 141 920 | 20. |
| 24 | 17 | 15 200 | 948 480 | 16. |
| 28 | 17 | 10 500 | 655 200 | 11. |
| Apr. 1 | 11 | 18 300 | 1 135 920 | 12. |

TABLE 3

RIVER DATA STATION II

| | $\frac{\text{Mg. } Cl^-}{\text{Sec.}}$ | Discharge $Ft.^3/Sec.$ | Discharge Lbs./Sec. | $\frac{\text{Lbs. } Cl^-}{\text{Sec.}}$ |
|---|---|---|---|---|
| Dec. 2 | 20 | 1 550 | 96 720 | 1.9 |
| 6 | 31 | 1 000 | 62 400 | 1.9 |
| 10 | 34 | 900 | 56 160 | 1.9 |
| 14 | 36 | 850 | 53 040 | 1.9 |
| 19 | 32 | 820 | 51 168 | 1.6 |
| 23 | 33 | 700 | 43 680 | 1.4 |
| 27 | 20 | 660 | 41 840 | .84 |
| Jan. 1 | 22 | 560 | 34 944 | .77 |
| 6 | 28 | 430 | 26 832 | .74 |
| 11 | 31 | 450 | 28 080 | .87 |
| 15 | 35 | 420 | 26 208 | .92 |
| 19 | 44 | 370 | 23 088 | 1.0 |
| 23 | 42 | 370 | 23 088 | .97 |
| 27 | 40 | 380 | 23 712 | .95 |
| 31 | 43 | 340 | 21 216 | .91 |
| Feb. 4 | 49 | 300 | 18 720 | .92 |
| 8 | 48 | 260 | 16 224 | .78 |
| 12 | 51 | 230 | 14 352 | .73 |
| 16 | 48 | 240 | 14 976 | .72 |
| 20 | 7 | 6 000 | 374 400 | 2.6 |
| 25 | 9 | 5 700 | 355 680 | 3.2 |

TABLE 3 - continued

RIVER DATA STATION II

| | $\frac{\text{Mg. } Cl^-}{\text{Sec.}}$ | Discharge $Ft.^3/Sec.$ | Discharge Lbs./Sec. | $\frac{\text{Lbs. } Cl^-}{\text{Sec.}}$ |
|---|---|---|---|---|
| Mar. 3 | 16 | 3 900 | 243 360 | 3.9 |
| 8 | 28 | 3 200 | 199 680 | 5.6 |
| 12 | 14 | 4 400 | 274 560 | 3.8 |
| 16 | 9 | 12 000 | 748 800 | 6.7 |
| 20 | 16 | 13 100 | 817 440 | 13. |
| 24 | 16 | 11 500 | 717 600 | 11. |
| 28 | 15 | 8 010 | 499 824 | 7.5 |
| Apr. 1 | 11 | 13 600 | 878 640 | 9.7 |

TABLE 4

RIVER DATA STATION III

| | Mg. $Cl^-$ / Sec. | Discharge $Ft.^3$/Sec. | Discharge Lbs./Sec. | Lbs. $Cl^-$ / Sec. |
|---|---|---|---|---|
| Dec. 2 | 12 | 743 | 46 363 | .56 |
| 6 | 24 | 340 | 21 216 | .51 |
| 10 | 23 | 486 | 30 326 | .70 |
| 14 | 20 | 260 | 16 224 | .32 |
| 19 | 29 | 300 | 18 720 | .54 |
| 23 | 20 | 400 | 24 960 | .50 |
| 27 | 17 | 450 | 28 080 | .48 |
| Jan. 1 | 15 | 410 | 25 584 | .38 |
| 6 | 25 | 180 | 11 232 | .28 |
| 11 | 22 | 160 | 9 984 | .22 |
| 15 | 29 | 150 | 9 360 | .27 |
| 19 | 24 | 130 | 8 112 | .20 |
| 23 | 24 | 140 | 8 736 | .21 |
| 27 | 24 | 140 | 8 736 | .21 |
| 31 | 24 | 130 | 8 112 | .20 |
| Feb. 4 | 27 | 110 | 6 864 | .19 |
| 8 | 14 | 100 | 6 340 | .09 |
| 12 | 28 | 110 | 6 864 | .19 |
| 16 | 34 | 130 | 8 112 | .28 |
| 20 | 2 | 18 000 | 1 123 200 | 2.2 |
| 25 | 7 | 5 750 | 358 800 | 2.5 |

TABLE 4 - continued

RIVER DATA STATION III

| | $\frac{\text{Mg. } Cl^-}{\text{Sec.}}$ | Discharge $\text{Ft.}^3/\text{Sec.}$ | Discharge Lbs./Sec. | $\frac{\text{Lbs. } Cl^-}{\text{Sec.}}$ |
|---|---|---|---|---|
| Mar. 3 | 14 | 3 310 | 206 544 | 2.9 |
| 8 | 22 | 2 010 | 125 424 | 2.8 |
| 12 | 11 | 5 590 | 348 816 | 3.8 |
| 16 | 8 | 9 720 | 606 528 | 4.9 |
| 20 | 13 | 4 210 | 262 704 | 3.4 |
| 24 | 11 | 3 170 | 197 808 | 2.2 |
| 28 | 11 | 2 340 | 146 250 | 1.6 |
| Apr. 1 | 10 | 4 860 | 303 264 | 3.0 |

TABLE 5

CHLORIDE GAINED BY THE DES MOINES RIVER AT DES MOINES, IOWA

| Date | Chloride Gained Lbs./Sec. | Date | Chloride Gained Lbs./Sec. |
|---|---|---|---|
| Dec. 2 | 1.3 | Feb. 4 | .43 |
| 6 | .95 | 8 | .31 |
| 10 | 1.5 | 12 | 1.4 |
| 14 | .07 | 16 | .84 |
| 19 | 1.0 | 20 | 2.0 |
| 23 | .39 | 25 | .68 |
| 27 | .93 | Mar. 3 | 1.1 |
| Jan. 1 | 1.6 | 8 | 1.1 |
| 6 | .96 | 12 | .42 |
| 11 | .79 | 16 | 4.7 |
| 15 | .37 | 20 | 4.0 |
| 19 | .27 | 24 | 2.4 |
| 23 | .48 | 28 | 2.0 |
| 27 | .66 | Apr. 1 | 2.8 |
| 31 | .35 | | |

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